DIFFERENTIAL THERMAL ANALYSIS OF THE REACTION PROPERTIES OF RAW AND RETORTED OIL SHALE WITH AIR

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INTRODUCTION

Oil shale can burn directly in the furnace to produce steam and electricity. Recently, in U.S.S.R. probably 75% of their oil shale which was excavated was burned in the boiler (1). In our country, there is only one small power station in Huang county, Shandong, using oil shale as a boiler fuel to produce electricity. When oil shale is pyrolyzed in retort to produce shale oil, the retorted shale char may be treated to react with air in order to supply heat energy for retorting. It is necessary to know the combustion properties of oil shale and its char in order to get kinetic equations.

The kinetics of the oil shale char combustion have been determined in a number of investigations (2-7). Most of the previous work has dealt with the combustion of oil shale char at high temperatures and in large samples. H. Y. Sohn (8) reported the results of an investigation to determine the intrinsic kinetics of the reaction between oxygen and char by using the TG method. In their experiment, the mass transfer and diffusional effects were eliminated by using a sufficiently high flow rate of gas and a small amount of solid particles spread thinly on the sample pan.

There are two discrete peaks in the DTA curve of oil shale combustion. It is easy to determine two reaction steps in the oil shale combustion. In this paper, the results of study to determine the kinetics of combustion of oil shale and its char by using DTA are reported.

EXPERIMENTAL SECTION

In this work, we used the Japanese "Rigaku" type thermal analysis apparatus. It is a combined apparatus of TGA and DTA. A platinum/platinum-rhodium thermocouple was used to measure the sample temperature. Both the sample and reference holders are made of platinum and are 5 mm in diameter and 2 mm thick.

Oil shale samples used were Fushun oil shale, Maoming oil shale, Huang county oil shale and Colorado oil shale. The char is a residue of oil shale which is retorted for 10 minutes at 510°C as in a Fischer Assay. The analysis data of oil shales and their chars used in this work are shown in Table I and Table II.

TABLE I

ANALYSIS DATA OF OIL SHALE USED IN THIS WORK (WT %)

| No. | Place | Fischer Analysis | | | | V | A | CO_2 | Organic Carbon % |
		Oil	Char	H_2O	Gas				
M812	Maoming (low grade)	4.5	85.2	8.0	2.3				13.52
M811[a]	Maoming (high grade)	8.8	84.1	3.7	3.4	22.8	71.9	1.4	17.47
M821	Maoming Jin Tang	8.2	84.0	3.8	4.0				17.27
F812[a]	Fushun	9.8	83.3	3.4	3.5	23.8	72.2	2.9	16.30
W821	Huang County	16.5	67.1	10.3	6.1	38.9	45	10.4	35.37
A811[a]	Colorado	6.4	89.9	1.8	1.9			15.0	

a. Analytical data were taken from Ass. Prof. Qin's work and allowed to use through his kindness.

In order to remove water which was contained in the oil shale, sample particles (-200 mesh) were dried for 2 hrs under 60°C and vacuum (600 mm Hg) condition.

TABLE II

CARBON AMOUNT IN THE CHAR USED IN THIS WORK (WT %)

No.	Place	Carbon %
M811C	Maoming oil shale (high grade) char	8.51
M821C	Maoming Jin Tang oil shale char	8.86
W821C	Huang county oil shale char	31.38

In order to compare the experimental parallel results, all experiments have been done with the same operating conditions:

Working atmosphere	air
Reference substance	α-Al_2O_3
Heating rate	10°C/min
DTA measuring range	$\pm$100 μv
Recording-paper speed	2.5 mm/min

THEORETICAL CONSIDERATION

The intrinsic kinetics for the reaction of a solid with a gas can be written as:

$$\frac{dx}{dt} = k \cdot f(P_A)(1-x)^n \qquad 1)$$

Where

t	–	time (min)
x	–	the fractional conversion of the solid reactant (%)
k	–	the reaction rate constant
$f(P_A)$	–	the dependence of rate on gaseous reactant concentration
n	–	order of reaction.

In this work, temperature is raised linearly with time during the run. Thus, we have:

$$T = T_O + a \cdot t, \quad dt = a \cdot dt \qquad 2)$$

T_O – initial temperature
a – heating rate

and k is no longer a constant in non-isothermal case:

$$k = A \cdot \exp(-E/RT) \qquad 3)$$

Combining Equation 1, 2 and 3 and integrating, we obtain

$$\int_O^x \frac{dx}{(1-x)^n} = \frac{A \cdot f(P_A)}{a} \int_{T_O}^T \exp(-E/RT)dT \cong \frac{A \cdot f(P_A)}{a} \int_O^T \exp(-E/RT)dT \qquad 4)$$

For greater values of E/RT, the integral on the right-hand side can be replaced by an approximate solution as follows:

$$\frac{A \cdot f(P_A)}{a} \int_O^T \exp(-E/RT)dT = \frac{A \cdot f(P_A)}{a} \cdot \frac{RT^2}{E}(1-\frac{2RT}{E})\exp(-E/RT) \qquad 4a)$$

The left-hand side can be integrated and combined with 4a. So, when n = 1,

$$-\ln(1-x) = \frac{A \cdot f(P_A)}{a} \cdot \frac{RT^2}{E}(1-\frac{2RT}{E})\exp(-E/RT) \qquad 5)$$

240

when $n \neq 1$

$$\frac{(1-x)^{1-n} - 1}{n-1} = \frac{A \cdot f(P_A)}{a} \cdot \frac{RT^2}{E} (1 - \frac{2RT}{E}) \exp(-E/RT)$$ 6)

H. Y. Sohn (1980) reported that the best value of A was obtained by using the value of T at $x = 0.5$ in the term

$$(1 - \frac{2RT}{E}) ,$$

and the first reaction order might be assumed so far the partial pressure of oxygen was concerned. Thus,

$$f(P_{O_2}) = P_{O_2}$$ 7)

A straight-line plot of

$$\ln(\frac{-\ln(1-x)}{T^2}) \text{ vs. } \frac{1}{T} \text{ (or } \ln\left[\frac{(1-x)^{1-n} - 1}{(n-1) \ T^2}\right] \text{vs. } \frac{1}{T})$$

will give birth to the apparent activation energy E and the straight-line interception with the ordinate axis. Substituting Equation 7 into the intercept thus obtained, we can calculate the preexponential factor A value.

RESULTS AND DISCUSSION

The Reaction of Oil Shale with Air

The DTA curves of six oil shales' combustion are shown in Figure 1. When oil shale reacts with air, there are two large peaks on the above mentioned DTA curve. The temperature of the first peak is 316°-356°C, the temperature of the second peak is 382°-454°C.

According to the obtained DTA curve, one can get the X - T curve (9, 10) shown in Figure 2.

A straight-line plot of

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] \text{ vs. } \frac{1}{T}$$

(shown in Figure 3) yields the apparent activation energy E and preexponential factor A. The kinetic equations of oil shale combustion are shown in Table III.

TABLE III

THE KINETIC EQUATIONS OF OIL SHALE COMBUSTION

No	k_1 (atm min)$^{-1}$	k_2 (atm min)$^{-1}$
M812	$4.750 \cdot 10^6 \exp(-18390/RT)$	$1.495 \cdot 10^3 \exp(-9462/RT)$
M811	$5.134 \cdot 10^5 \exp(-16420/RT)$	$1.593 \cdot 10^3 \exp(-9833/RT)$
M821	$7.387 \cdot 10^4 \exp(-14720/RT)$	$2.866 \cdot 10^3 \exp(-10880/RT)$
F811	$3.765 \cdot 10^4 \exp(-14080/RT)$	$2.08 \cdot 10^2 \exp(-7887/RT)$
W821	$7.806 \cdot 10^3 \exp(-12320/RT)$	$9.933 \cdot 10^3 \exp(-12800/RT)$
A811	$k=3.786 \cdot 10^5 \exp(-15890/RT)$	

Table III shows that most of oil shales used in this work have two combustion kinetic Equations. It indicates that there are two reactions in the oil shale combustion process. But, for Colorado oil shale, the two peaks are too close. Only one combustion kinetic equation to express its combustion property can be formulated.

The Reaction of Char with Air

The DTA curves of char combustion are shown in Figure 4. It can be seen from Figure 4 that there is only one peak for each oil shale, the obtained DTA curve. The temperatures of the peaks lie in the range from 360°C to 410°C.

According to the obtained DTA curve, one can draw a plot of

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] \text{ vs. } \frac{1}{T}$$

and get their apparent activation energy E and preexponential factor A (the same method mentioned above).

Table IV displays these obtained kinetic parameters. It can be seen that the combustion rate of Colorado oil shale char is extraordinarily faster than that of other chars; the combustion rate of two Maoming oil shale chars is found to be the same and the combustion rate of Huang county oil shale char is faster than Maoming oil shale char.

TABLE IV

THE KINETIC PARAMETERS OF CHAR COMBUSTION

No.	Correlation Coefficient	n	k (atm min)$^{-1}$
M811C-2	0.9950	1	$1.267 \cdot 10^4 \exp(-13360/RT)$
M821C	0.9942	1	$9.872 \cdot 10^3 \exp(-13010/RT)$
W821C	0.9944	1	$6.380 \cdot 10^3 \exp(-12180/RT)$
A811C	0.9952	1	$2.190 \cdot 10^6 \exp(-18250/RT)$

The Effect of the Sample Quantity on the Experiment

In order to inspect the effect of diffusion on the experiment, several sample quantities in milligrams of Maoming oil shale char were taken in this work. Results are in Table V.

TABLE V

THE RELATION BETWEEN SAMPLE QUANTITIES AND SAMPLE THICKNESS

No.	Sample Quantity (mg)	Sample Thickness in the Holder (mm)
M811C-1	6.3	0.38
M811C-2	9.1	0.54
M811C-3	18.1	1.08
M811C-4	27.0	1.62

Figure 5 shows the TG-DTA curve of four sample quantities of Maoming oil shale char. It can be seen from Figure 5 that the obtained peak temperatures are the same (about 438°C). It means that the peak temperature relates only to the sample property and bears no relationship to the sample quantity. According to Figure 5, one can get their kinetic parameters (same method as mentioned).

Table VI displays the obtained combustion kinetic parameters of four samples of Maoming oil shale char. It can be seen from Figure 5 and Table VI that, when the sample quantity is between 6.3 and 18 mg, the obtained kinetic parameters are nearly the same. But, when the sample quantity is 27 mg, its kinetic parameter differs greatly from the others. An effect of diffusion can be elicited only when the sample amount is more than 27 mg.
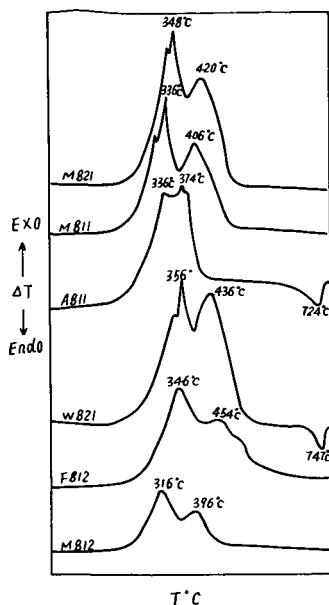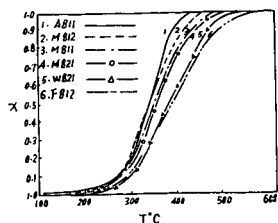
Figure 1. Six oil shale combustion
DTA curves

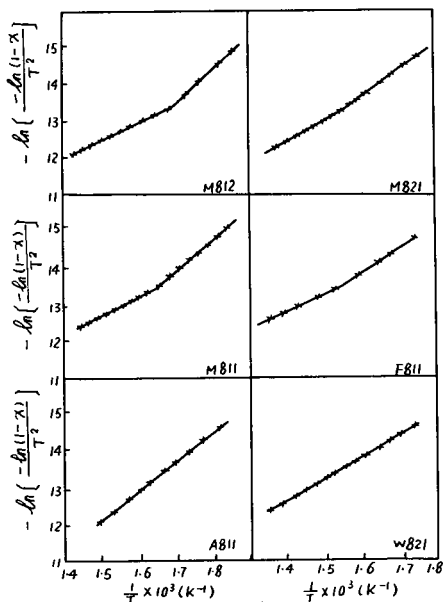Figure 2. X-T curve of six
samples of oil shale.

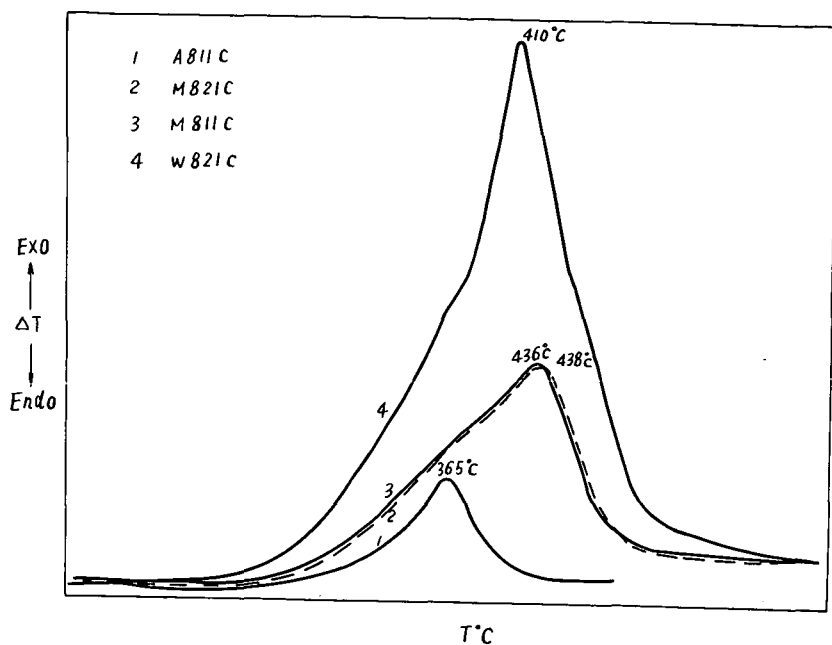Figure 3. A plot of $\ln\left[\dfrac{-\ln(1-x)}{T^2}\right]$ vs. $\dfrac{1}{T}$

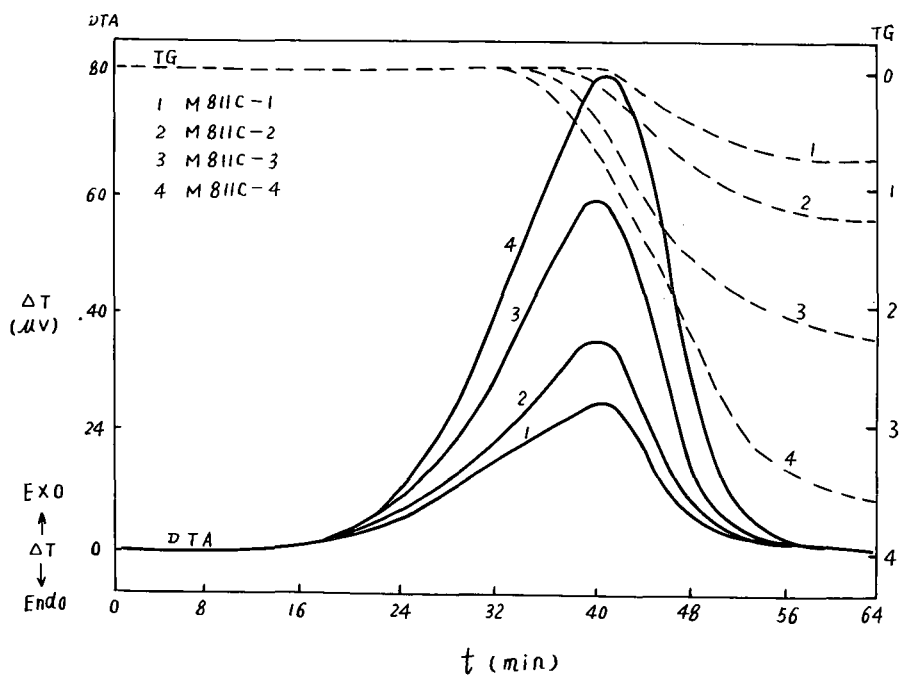Figure 4. The combustion DTA curves of the chars used in this work

Figure 5. The TG-DTA curve of several sample amount of Maoming oil shale char

244

TABLE VI

THE COMBUSTION KINETICS OF SEVERAL SAMPLE AMOUNTS OF MAOMING OIL SHALE CHAR

No.	Correlation Coefficient	n	K
M811C-1	0.9979	1	$1.754 \cdot 10^4 \exp(-13770/RT)$
M811C-2	0.9950	1	$1.267 \cdot 10^4 \exp(-13360/RT)$
M811C-3	0.9960	1	$1.018 \cdot 10^4 \exp(-13090/RT)$
M811C-4	0.9954	1	$4.990 \cdot 10^3 \exp(-12210/RT)$

CONCLUDING REMARKS

There are two large peaks on the oil shale combustion DTA curve, but there is only one peak on its char combustion DTA curve.

Oil shale and its char combustion reaction is of the first order. The kinetic parameters of six oil shales and their char used in this work are shown in Tables III and IV. It indicates that Colorado oil shale and its char combustion rate is the fastest while Fushun oil shale and its char combustion rate is the slowest among the six oil shales used in this work.

Under experimental conditions as mentioned, when the sample quantity is less than 18 mg and the temperature is below 500°C, the sample quantity have no significant effect on the combustion rate.

ACKNOWLEDGMENT

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